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(54) **Method of processing camera speed silver chloride photographic elements using peroxide bleaching solutions**

(57) Camera speed color photographic elements are effectively bleached using a peroxide bleaching solution containing critical amounts of peroxide and chloride ion. These elements have predominantly chloride silver halide emulsions that contain less than 2% iodide ion, and are substantially free of a bleaching rate retarding amount of a development inhibitor having a free valence that binds to silver. No vesiculation in the processed element is observed after bleaching.

**EP 0 747 764 A1**

## Description

The present invention relates generally to the processing of color photographic elements in photography. More particularly, it relates to a method of using peroxide bleaching solutions to process camera speed photographic elements containing predominantly silver chloride emulsions.

The basic image-forming process of color photography comprises exposing a silver halide photographic recording material to light, and chemically processing the material to reveal a useful image. Such processing typically includes color development to reduce silver halide to metallic silver and to form one or more organic dyes.

Developed silver is removed by sequential steps of oxidation to a silver salt (bleaching step), and dissolution and washing out of that silver salt from the element (fixing step). In alternative processes, these two steps are combined in what is known as a bleach-fixing step. Other optional steps may be included in the processing, including one or more black and white development, chemical fogging, development stop, washing, accelerating and stabilizing steps.

In many instances, a customer captures a latent image on what is known as an "originating" element that in most instances is a "camera speed" photographic color negative or motion picture negative film. The resulting image is then used to modulate the exposure of a light sensitive "display" element in a printer. The "display" element may be, for example, a color paper, an intermediate film or a motion picture projection film. The exposed display element is then processed appropriately to form a useful color image that duplicates the original image captured by the customer.

Originating elements, such as camera speed films, are typically designed to allow good exposure with available light under a wide variety of lighting conditions. That is, they are designed to have good sensitivity and dynamic range. Recent advances in emulsion science have made it possible to create camera speed photographic films having predominantly silver chloride emulsions, and especially silver chloride emulsions having tabular grains. For example, representative tabular grain emulsions having {111} major faces are described in US-A-5,176,991, US-A-5,176,992, US-A-5,178,997, US-A-5,178,998, US-A-5,183,732, US-A-5,185,239, US-A-5,217,858, US-A-5,221,602, US-A-5,252,452 and US-A-5,272,052. Other suitable emulsions are {100} tabular silver chloride emulsions that are described, for example, in US-A-5,264,337, US-A-5,275,930, US-A-5,292,632, US-A-5,314,798 and US-A-5,320,938.

Methods of processing photographic elements containing such emulsions are described, for example, in US-A-5,443,943.

The most common photographic bleaching solutions for processing originating or camera speed elements contain complexes of ferric ion and various organic ligands as bleaching agents. Such solutions are well known in the art, including *Research Disclosure*, No. 365, publication 36544, pages 501-541, September 1994 (referred to hereinafter as "*Research Disclosure*"). While such ferric complexes are highly effective for the intended purpose, there are considerable environmental concerns with both the iron salts and any non-biodegradable chelating agents used to form some of the known complexes. It would be desirable to reduce or eliminate their use. Hence, there is a considerable effort in the photographic industry to design bleaching solutions that are more compatible with the environment.

Peracid bleaching solutions, such as those containing peroxide, persulfate, perborate, perphosphate, perhalogen, percarboxylic acid or percarbonate bleaching agents, offer an alternative to the ferric complex bleaching solutions. They may be less expensive and usually present lower chemical and biological demands on the environment since their by-products can be less harmful.

A common peracid bleaching solution is one containing a persulfate bleaching agent. Use of persulfate salts enables the use of chloride ion as a rehalogenating agent, yielding substantial fixing benefits. In the case of ferric catalyzed persulfate bleaching solutions, such as those described in US-A-5,460,924, iron concentration is reduced compared to ferric complex bleaching solutions, and biodegradable ligands are employed.

Nevertheless, persulfate salts used as bleaching agents increase the concentration of sulfate salts in photographic processing effluent. Such salts have been associated with degradation of concrete sewer pipes. Some persulfate bleaching solutions are free of iron, but they bleach slowly and thus require the presence of a bleaching accelerator in a bleaching prebath. The most common bleaching accelerators are thiols that have offensive odors.

From an environmental perspective, the most attractive bleaching agent is a peroxide, such as hydrogen peroxide, or one of its precursors. When it oxidizes silver in a photographic element, hydrogen peroxide is converted to water. Like a persulfate bleaching agent, hydrogen peroxide enables the use of chloride ion as a rehalogenating agent so that the fixing time or the concentration of fixing agent is reduced from that normally required when bromide ion is used as a rehalogenating agent.

These considerable incentives to evaluate and use peroxide as a bleaching agent have spawned considerable research relating to peroxide bleaching, as described for example, in US-A-4,277,556, US-A-4,301,236, US-A-4,454,224, US-A-4,717,649, WO-A-92/01972, WO-A-92/07300, WO-A-93/11459 and EP-A-0 428 101.

In particular, EO-A-92/07300 and EP-A-0 428 101 describe the use of peroxide compositions for bleaching high chloride photographic elements. Such compositions include up to 0.4 mol chloride ions per liter of bleaching solution and have a pH of from 5 to 11. These particular bleaching solutions, however, cause vesiculation (or blistering from evolution of oxygen) in the processed elements. Of the methods that avoid vesiculation, none provide complete bleaching within a useful period of time.

There remains a need, however, for a rapid and effective method of processing predominantly silver chloride originating (or camera speed) photographic elements using a peroxide bleaching solution, but without vesiculation.

The present invention provides a method for processing an imagewise exposed and developed originating color photographic element that:

- a) has at least one silver halide emulsion layer having predominantly chloride ion as the halide, and less than 2% iodide ion, based on total silver halide, and
- b) is substantially free of a bleaching rate retarding amount of a development inhibitor having a free valence that binds to silver,

the method comprising bleaching the element with a bleaching solution comprising:

a peroxide bleaching agent present in an amount of at least 0.5 mol/l, and  
chloride ion present in an amount of at least 0.35 mol/l.

Rapid bleaching of camera speed photographic elements is provided with the present invention. Moreover, bleaching is complete and accompanied by reduced or no vesiculation. These advantages are achieved by a combination of a particular type of photographic emulsion in the element and specific peroxide bleaching solution. More particularly, the element is predominantly a silver chloride element containing little or no iodide ion in the emulsions, and is substantially free of a bleaching rate retarding amount of a development inhibitor having a free valence that binds to silver. The bleaching solution has at least 0.5 mol/l of the peroxide bleaching agent, and at least 0.35 mol/l of chloride ion as rehalogenating agent.

Peroxide bleaching solutions useful in the practice of this invention comprise a conventional peroxide bleaching agent including hydrogen, alkali and alkaline earth salts of peroxide, or a compound that releases or generates hydrogen peroxide. Such hydrogen peroxide precursors include perborate, perphosphate, percarbonate, percarboxylate and hydrogen peroxide urea.

In addition, hydrogen peroxide can be generated on site by electrolysis of an aqueous solution. Examples of peroxide bleaching solutions are described, for example, in *Research Disclosure*, publication 36544 (noted above). Hydrogen peroxide is the preferred bleaching agent.

The amount of peroxide (or its precursor) is generally from 0.35 to 5 mol/l. Preferably, it is present at from 0.6 to 2.5 mol/l of bleaching solution.

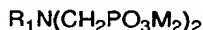
Chloride ions can be supplied to the bleaching solution as part of a simple inorganic salt, such as an ammonium or alkali metal salt (for example, sodium chloride, potassium chloride, lithium chloride and ammonium chloride). In addition, they can be supplied as salts of organic counterions such as tetraalkylammonium chloride. Preferred salts are sodium chloride and potassium chloride.

Chloride ion concentration is from 0.35 to 1 mol/l. Preferably, it is present in an amount of from 0.35 to 0.75 mol/l.

The bleaching solutions used in this invention are quite simple, having only two essential components, the peroxide bleaching agent and chloride ions. Other optional and preferred components include a buffer, and a sequestering agent, such as an organic phosphonic acid or carboxylic acid, or a salt thereof, each of which is defined below in an amount of at least 0.0005 mol/l.

The peroxide bleaching solution is alkaline, having a pH within the general range of from 7 to 13, with a pH of from 8 to 12 being preferred, and a more preferred range being from 9 to 11. The pH can be provided by adding a conventional weak or strong base, and can be maintained by the presence of one or more suitable buffers including, but not limited to, sodium carbonate, potassium carbonate, sodium borate, potassium borate, sodium phosphate, calcium hydroxide, sodium silicate,  $\beta$ -alaninediacetic acid, arginine, asparagine, ethylenediamine, ethylenediaminetetraacetic acid, ethylenediaminedisuccinic acid, glycine, histidine, imidazole, isoleucine, leucine, methyliminodiacetic acid, nicotine, nitrilotriacetic acid, piperidine, proline, purine and pyrrolidine. Sodium carbonate and potassium carbonate are preferred.

The bleaching solution of this invention can comprise one or more organic phosphonic acids or salts thereof. Generally such compounds are represented by structure (I):



or (II):



wherein  $R_1$  is hydrogen, a substituted or unsubstituted alkyl group of 1 to 12 carbon atoms (such as methyl, hydroxymethyl, ethyl, isopropyl, *t*-butyl, hexyl, octyl, nonyl, decyl, benzyl, 4-methoxybenzyl, beta-phenethyl, *o*-octamidobenzyl) or

beta-phenethyl), a substituted or unsubstituted alkylaminoalkyl group (wherein the alkyl portion of the group is as defined above, such as methylaminomethyl or ethylaminoethyl), a substituted or unsubstituted alkoxyalkyl group of 1 to 12 carbon atoms (such as methoxymethyl, methoxyethyl, propoxyethyl, benzyloxy, methoxymethylenemethoxymethyl or *t*-butoxy), a substituted or unsubstituted aryl group of 6 to 10 carbon atoms (such as phenyl, naphthyl, 4-methylphenyl, 4-hydroxyphenyl, 3-methoxyphenyl, *o*-tolyl, *m*-tolyl or *p*-carboxyphenyl), a substituted or unsubstituted cycloalkyl group of 5 to 10 carbon atoms (such as cyclopentyl, cyclohexyl, cyclooctyl or 4-methylcyclohexyl), or a substituted or unsubstituted 5- to 10-membered heterocyclic group having one or more nitrogen, oxygen or sulfur atoms in the ring besides carbon atoms [such as pyridyl, pyrimidyl, pyrrolyldimethyl, pyrrolyldibutyl, benzothiazolylmethyl, tetrahydroquinolylmethyl, 2-pyridinylmethyl, 4-(*N*-pyrrolidino)butyl or 2-(*N*-morpholino)ethyl].

$R_2$  is hydrogen, a substituted or unsubstituted alkyl group of 1 to 12 carbon atoms (as defined above), a substituted or unsubstituted aryl group of 6 to 10 carbon atoms (as defined above), a substituted or unsubstituted cycloalkyl group of 5 to 10 carbon atoms (as defined above), a substituted or unsubstituted 5- to 10-membered heterocyclic group (as defined above),  $-PO_3M_2$  or  $-CHR_4PO_3M_2$ .

$R_3$  is hydrogen, hydroxyl, a substituted or unsubstituted alkyl group of 1 to 12 carbon atoms (defined above) or  $-PO_3M_2$ .

$R_4$  is hydrogen, hydroxyl, a substituted or unsubstituted alkyl group of 1 to 12 carbon atoms (as defined above) or  $-PO_3M_2$ .

$M$  is hydrogen or a water-soluble monovalent cation imparting water-solubility such as an alkali metal ion (for example sodium or potassium), or ammonium, pyridinium, triethanolammonium, triethylammonium ion or others readily apparent to one skilled in the art. The two cations in each molecule do not have to be the same. Preferably,  $M$  is hydrogen, sodium or potassium.

In defining the substituted monovalent groups above, useful substituents include an alkyl group, hydroxy, sulfo, carbonamido, sulfonamido, sulfamoyl, sulfonato, thialkyl, alkylcarbonamido, alkylcarbonyl, alkylsulfonamido, alkylsulfamoyl, carboxyl, amino, halo (such as chloro or bromo) sulfono, or sulfoxo, alkoxy of 1 to 5 carbon atoms (linear or branched),  $-PO_3M_2$ ,  $-CH_2PO_3M_2$  or  $-N(CH_2PO_3M_2)_2$ , wherein the alkyl (linear or branched) for any of these groups has 1 to 5 carbon atoms.

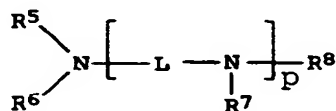
Representative phosphonic acids useful in the practice of this invention include the compounds listed in EP 0 428 101A1 (page 4), as well as the following compounds:

ethylenediamine-*N,N,N',N'*-tetramethylenephosphonic acid, nitrilo-*N,N,N*-trimethylenephosphonic acid, 1,2-cyclohexanediamine-*N,N,N',N'*-tetramethylenephosphonic acid, *o*-carboxyaniline-*N,N*-dimethylenephosphonic acid, propylamine-*N,N*-dimethylenephosphonic acid, 4-(*N*-pyrrolidino)butylamine-*N,N*-bis(methylenephosphonic acid), 1,3-diamino-2-propanol-*N,N,N',N'*-tetramethylenephosphonic acid, 1,3-propanediamine-*N,N,N',N'*-tetramethylenephosphonic acid, 1,6-hexanediamine-*N,N,N',N'*-tetramethylenephosphonic acid, *o*-acetamidobenzylamine-*N,N*-dimethylenephosphonic acid, *o*-toluidine-*N,N*-dimethylenephosphonic acid, 2-pyridylmethylamine-*N,N*-dimethylenephosphonic acid, 1-hydroxyethane-1,1-diphosphonic acid, diethylenetriamine-*N,N,N',N',N''*-penta(methylenephosphonic acid), 1-hydroxy-2-phenylethane-1,1-diphosphonic acid, 2-hydroxyethane-1,1-diphosphonic acid, 1-hydroxyethane-1,1,2-triphosphonic acid, 2-hydroxyethane-1,1,2-triphosphonic acid, ethane-1,1-diphosphonic acid, and ethane-1,2-diphosphonic acid.

Most useful are 1-hydroxyethylidene-1,1-diphosphonic acid, nitrilo-*N,N,N*-trimethylenephosphonic acid, diethylenetriamine-*N,N,N',N',N''*-penta(methylenephosphonic acid) or salts thereof. The first compound is most preferred.

The amount of organic phosphonic acid useful in the practice of the invention can be at least 0.0005 mol/l and generally up to 0.03 mol/l. An amount of from 0.0025 to 0.012 mol/l is preferred.

Instead of, or in addition to, the organic phosphonic acids (or salts) described above, the peroxide bleaching solution can also contain one or more aminocarboxylic acids (or salts thereof) that contain a tertiary amine (identified above as a "tertiary amino carboxylic acid"). These compounds can be represented by the structure (III):

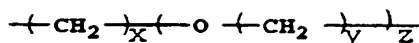


wherein  $R^5$ ,  $R^6$ ,  $R^7$  and  $R^8$  are independently hydroxyalkyl of 1 to 3 carbon atoms, or carboxyalkyl of 2 to 4 carbon atoms, provided at least one of these groups is carboxyalkyl. The alkyl groups are substituted and can be linear or branched. The alkyl groups can also be hydroxy-substituted. Preferably, the hydroxyalkyl or carboxyalkyl groups have methyl or ethyl groups.

In structure (III),  $p$  is 0 or an integer of 1 to 3.

$L$  is a substituted or unsubstituted alkylene group of 2 to 4 carbon atoms (linear or branched, and substituted with

hydroxy or carboxy). L can also be a



group wherein x and y are independently integers of 2 to 4, and z is an integer of 1 to 3. Moreover, L can be a 6-membered cyclic substituted or unsubstituted alkylene group (optionally substituted with hydroxy or carboxy) or a substituted or unsubstituted arylene group of 6 to 10 carbon atoms (such as phenylene or naphthylene, optionally substituted with hydroxy or carboxy). Preferably, the compound of Structure (III) has more than one carboxy group.

Representative tertiary aminocarboxylic acids useful in this invention include diethylenetriaminepentaacetic acid and 2-hydroxypropylenediaminetetraacetic acid. The first compound is preferred.

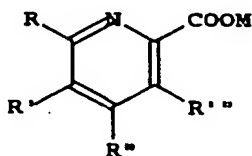
The amount of such tertiary aminocarboxylic acids useful in the bleaching solution can be at least 0.0005 mol/l and generally up to 0.03 mol/l, with from 0.0025 to 0.012 mol/l being preferred.

Still another optional carboxylic acid in the bleaching solution is one that generally comprises at least one carboxyl group and an aromatic nitrogen heterocycle. They are water-soluble and preferably biodegradable.

More specifically, this group of carboxylic acids includes substituted or unsubstituted 2-pyridinecarboxylic acids and substituted or unsubstituted 2,6-pyridinedicarboxylic acids (or equivalent salts). The substituents which may be on the pyridinyl ring include substituted or substituted alkyl, substituted or unsubstituted cycloalkyl or substituted or unsubstituted aryl groups (as defined above for structures I-II), hydroxy, nitro, sulfo, amino, carboxy, sulfamoyl, sulfonamide, phospho, halo or any other group that does not interfere with metal complexation or solubility. The substituents can also be the atoms necessary to form a 5- to 7-membered fused ring between any of the positions of the pyridinyl nucleus.

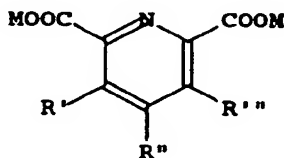
The preferred acids of this type are represented by the following structures:

(IV)



and

(V)



wherein R, R', R'' and R''' are independently hydrogen, a substituted or unsubstituted alkyl group of 1 to 5 carbon atoms (as defined above), a substituted or unsubstituted aryl group of 6 to 10 carbon atoms (as defined above), a substituted or unsubstituted cycloalkyl group of 5 to 10 carbon atoms (as defined above), hydroxy, nitro, sulfo, amino, carboxy, sulfamoyl, sulfonamido, phospho or halo (such as chloro or bromo), or

any two of R, R', R'' and R''' can comprise the carbon atoms necessary to form a substituted or unsubstituted 5 to 7-membered ring fused with the pyridinyl nucleus. M is as defined above.

Preferably, R, R', R'' and R''' are independently hydrogen, hydroxy or carboxy. The most preferred compounds are unsubstituted 2-pyridinecarboxylic acid and 2,6-pyridinedicarboxylic acid or salts thereof.

The amount of this type of acid useful in the practice of this invention is at least 0.001 and generally up to 0.05 mol/l. Preferred amounts are from 0.002 to 0.035 mol/l.

Still another optional carboxylic acid useful in the bleaching solution is a polyaminocarboxylic acid that has at least

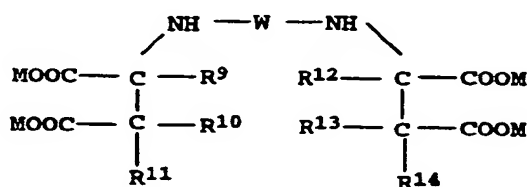
one secondary amino group at a pH of from 8 to 11. The compound also has at least two carboxyl groups (polydentate), or their corresponding salts. Such acids can be bidentate, tridentate, tetradentate, pentadentate and hexadentate ligands. These acids must be water-soluble also, and are preferably biodegradable (defined below).

More specifically, these compounds include alkylenediaminetetracarboxylic acids having at least one secondary nitrogen atom, and alkylenediaminepolycarboxylic acids having at least one secondary nitrogen atom.

Representative useful classes of such acidic compounds are defined below in reference to structures (VI)-(X), although it should be recognized that the invention is not limited in practice to these compounds.

Thus, the compounds can have any of the following structures:

(VI)



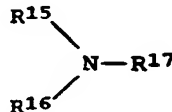
wherein

$\text{R}^9$ ,  $\text{R}^{10}$ ,  $\text{R}^{11}$ ,  $\text{R}^{12}$ ,  $\text{R}^{13}$  and  $\text{R}^{14}$  are independently hydrogen, hydroxy, a linear or branched substituted or unsubstituted alkyl group of 1 to 5 carbon atoms (such as methyl, ethyl, propyl, isopropyl, *n*-pentyl, *t*-butyl and 2-ethylpropyl), a substituted or unsubstituted cycloalkyl group of 5 to 10 carbon atoms in the ring (such as cyclopentyl, cyclohexyl, cycloheptyl and 2,6-dimethylcyclohexyl), or a substituted or unsubstituted aryl group having 6 to 10 carbon atoms in the aromatic nucleus (such as phenyl, naphthyl, tolyl and xylyl),

M is as defined above,

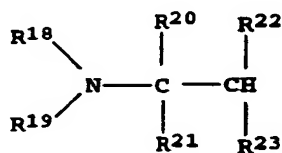
W is a covalent bond or a divalent substituted or unsubstituted aliphatic linking group (defined below),

(VII)



wherein at least two of  $\text{R}^{15}$ ,  $\text{R}^{16}$  and  $\text{R}^{17}$  are a carboxymethyl groups (or equivalent salts), and the third group is hydrogen,

(VIII)

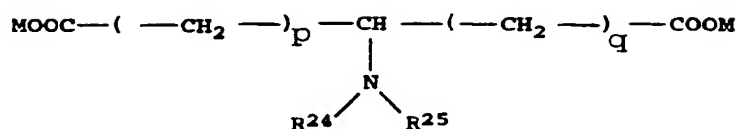


wherein

one of  $\text{R}^{18}$  and  $\text{R}^{19}$  is hydrogen and the other is substituted or unsubstituted carboxymethyl group (or equivalent salts) or 2-carboxyethyl group (or equivalent salts), and

$\text{R}^{20}$ ,  $\text{R}^{21}$ ,  $\text{R}^{22}$  and  $\text{R}^{23}$  are independently hydrogen, a substituted or unsubstituted alkyl group of 1 to 5 carbon atoms (as defined above), hydroxy, carboxy, carboxymethylamino, or a substituted or unsubstituted carboxymethyl group (or equivalent salts), provided that only one of  $\text{R}^{20}$ ,  $\text{R}^{21}$ ,  $\text{R}^{22}$  and  $\text{R}^{23}$  is carboxy, carboxymethylamino, or a substituted or unsubstituted carboxymethyl group (or equivalent salts),

(IX)



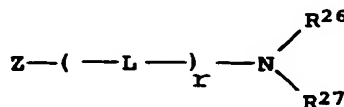
wherein

one of  $\text{R}^{24}$  and  $\text{R}^{25}$  is hydrogen and the other is a substituted or unsubstituted alkyl group of 1 to 5 carbon atoms (as defined above), substituted or unsubstituted hydroxyethyl group, substituted or unsubstituted carboxymethyl or 2-carboxyethyl group (or equivalent salts),

M is as defined above, and

p and q are independently 0, 1 or 2 provided that the sum of p and q does not exceed 2, or

(X)



wherein

Z represents a substituted or unsubstituted aryl group of 6 to 10 carbon atoms in the nucleus (as defined above) or a substituted or unsubstituted heterocyclic group having 5 to 7 carbon, nitrogen, sulfur and oxygen atoms in the nucleus (such as furanyl, thiofuranyl, pyrrolyl, pyrazolyl, triazolyl, dithiolyl, thiazolyl, oxazolyl, pyranlyl, pyridyl, piperidinyl, pyrazinyl, triazinyl, oxazinyl, azepinyl, oxepinyl and thiapinyl),

L is a divalent substituted or unsubstituted aliphatic linking group (defined below),

one of  $\text{R}^{26}$  and  $\text{R}^{27}$  is hydrogen and the other is a substituted or unsubstituted alkyl group of 1 to 5 carbon atoms (as defined above), a substituted or unsubstituted carboxyalkyl group of 2 to 4 carbon atoms (such as substituted or unsubstituted carboxymethyl or carboxyethyl or equivalent salts) or a hydroxy-substituted carboxyalkyl group of 2 to 4 carbon atoms (or equivalent salts), and

r is 0 or 1.

The "divalent substituted or unsubstituted aliphatic linking group" in the definition of "W" and "L" noted above includes any nonaromatic linking group comprised of one or more alkylene, cycloalkylene, oxy, thio, amino or carbonyl groups that form a chain of from 1 to 6 atoms. Examples of such groups include alkylene, alkyleneoxyalkylene, alkylencycloalkylene, alkylenethioalkylene, alkyleneaminoalkylene, alkylencarbonyloxyalkylene, all of which can be substituted or unsubstituted, linear or branched, and others that would be readily apparent to one skilled in the art.

As used herein, the terms "biodegradable" or "biodegradability" are defined such that at least 80% of dissolved carbon is lost within 21 days under conditions specified in DIN Standard 38,412 [German Standard Method for the Examination of Water, Waste Water and Sludge, Bioassays (Group L), Determination of Biodegradability, Static Test (L25)].

In defining the "substituted or unsubstituted" monovalent and divalent groups for the structures (I) - (X) noted above, by "substituted" is meant the presence of one or more substituents on the group, such as an alkyl group of 1 to 5 carbon atoms (linear or branched), hydroxy, carboxy, sulfo, sulfonato, thioalkyl, alkylcarbonamido, alkylcarbamoyle, alkylsulfonamido, alkylsulfamoyl, carbonamido, sulfonamido, sulfamoyl, amino, halo (such as chloro or bromo), sulfono (-SO<sub>2</sub>Alk) or sulfoxo [-S(O)Alk] wherein Alk is a branched or linear alkyl group of 1 to 5 carbon atoms.

In reference to the foregoing structures (VI)-(X), preferred definitions of groups are as follows:

M is hydrogen, ammonium, lithium, sodium or potassium,

$\text{R}^9$ ,  $\text{R}^{10}$ ,  $\text{R}^{11}$ ,  $\text{R}^{12}$ ,  $\text{R}^{13}$  and  $\text{R}^{14}$  are independently hydrogen, hydroxy or methyl,

W is a covalent bond or a substituted or unsubstituted alkylene group of 1 to 3 carbon atoms,

one of  $\text{R}^{18}$  and  $\text{R}^{19}$  is carboxymethyl,

$\text{R}^{20}$ ,  $\text{R}^{21}$ ,  $\text{R}^{22}$  and  $\text{R}^{23}$  are independently hydrogen, carboxymethyl or carboxy,

one of  $\text{R}^{24}$  and  $\text{R}^{25}$  is methyl or carboxymethyl,

Z represents 2-pyridyl or 2-imidazolyl,

L is substituted or unsubstituted alkylene of 1 to 3 carbon atoms,

one of  $\text{R}^{26}$  and  $\text{R}^{27}$  is 2-carboxyethyl or carboxymethyl, and

r is 1.

More preferred compounds of these structures are N,N-ethylenediaminedisuccinic acid, N,N-ethylenediaminediacetic acid, and N-(2-carboxyethyl)aspartic acid.

Besides those acids specifically defined in the foregoing description, there is considerable literature that describes additional useful organic phosphonic and carboxylic acids, such as EPA 0 567 126, US-A-5,250,401 and US-A-5,250,402.

Other addenda commonly added to peroxide bleaching solutions can also be included, such as corrosion inhibitors, optical whitening agents, defoaming agents, calcium sequestrants, peroxide stabilizers, radical scavengers, halogen scavengers, and other materials readily apparent to one skilled in the art.

The color photographic elements to be processed using the present invention are "originating" elements that allow good exposure with available light under a wide variety of lighting conditions. They provide good speed with low graininess, and are considered camera speed films because of their usefulness in consumer photography. At a minimum, the elements have an ISO speed rating of 25 or greater, with a speed greater than ISO 50 being preferred.

The speed or sensitivity of color negative photographic films, for example, is inversely related to the exposure required to enable the attainment of a specified density above fog after processing. Photographic speed for color negative films with a gamma of 0.65 has been specifically defined by the American National Standards Institute (ANSI) as ANSI Standard Number PH 2.27- 1979 (ASA speed) and relates to the exposure levels required to enable a density of 0.15 above fog in the green light sensitive and least sensitive recording unit of a multicolor negative film. This definition conforms to the International Standards Organization (ISO) film speed rating.

The photographic elements processed according to the present invention have predominantly chloride ion as the halide ion, based on the total silver halide. This means that at least 50 mol% of the total emulsion halide ions is chloride ion. Thus, the emulsion can be silver chloride, silver bromochloride, silver iodobromochloride, silver iodochloride, or any combination thereof as long as at least 50 mol% of the total is silver chloride. Preferably, the emulsion contains at least 70 mol% chloride ion, with over 90 mol% chloride ion being more preferred.

In addition, the total amount of silver iodide in the emulsions of the photographic element must be less than 2 mol%, and preferably less than 1%.

The total amount of coated silver in an originating element can be from 0.5 to 10 g/m<sup>2</sup> with less than 7 g/m<sup>2</sup> being preferred, and from 1 to 4 g/m<sup>2</sup> being more preferred.

The originating elements processed according to this invention contain at least one radiation sensitive silver halide emulsion containing a dispersing agent and a predominantly chloride silver halide grain population as described above. In a preferred embodiment, at least 50% of the total grain projected area of that population is accounted for by tabular grains that are bounded by (100) major faces having adjacent edge ratios of less than 10. In addition, each grain has an aspect ratio of at least 2. These tabular grains are intrinsically stable and do not require the presence of various sulfur-containing stabilizers known in the art that may restrain development.

It has been further discovered that these elements must be substantially free of certain development inhibitors having a free valence that binds to silver. Such development inhibitors typically comprise a silver halide binding group having a sulfur, selenium or tellurium with a free valence that can form a bond with silver atoms, as well as a ballast moiety. The presence of such compounds appears to slow down the rate of desilvering (that is, bleaching) in the elements described herein, as compared to other classes of development inhibitors or where development inhibitors are completely absent.

By "substantially free" is meant that the element at bleaching contains no more than 0.003 mol of such development inhibitors per mole of silver and silver halide. In a preferred embodiment, the quantity of such development inhibitors is less than 0.001 mol per mol of coated silver and silver halide. These relative quantities are best assured by controlling both the quantity of development inhibitor releasing (DIR) compounds and unblocked development inhibitors having the undesired characteristics as well as the quantity of silver halide during the preparation of the light sensitive element. In other words, before photographic development, the element should contain less than 0.003 mol total of both DIR compounds capable of releasing a development inhibitor having a free sulfur valence that binds to silver and development inhibitors having a free sulfur valence that binds to silver, per mol of silver halide. In a more preferred embodiment, this ratio should be less than 0.001 mol per mol of silver halide. In such amounts, the development inhibitors do not significantly retard silver bleaching.

In the practice of this invention, it is preferred to use development inhibitors having a heterocyclic nitrogen as a silver binding group, such as oxazoles, thiazoles, diazoles, triazoles, oxadiazoles, thiadiazoles, oxathiazoles, thiatriazoles, benzotriazoles, tetrazoles, benzimidazoles, indazoles, isindazoles, benzodiazoles or benzisodiazoles.

As noted above, the preferred emulsions used in this invention contain tabular grains. The following description of such grains is representative and is not meant to be exhaustive. Considerable details such emulsions are provided in US-A-5,443,943.

To identify tabular grains having {100} crystal faces, it is necessary to determine for each grain its ratio of "equivalent circular diameter" (ECD) to thickness (t), that is, ECD/t. ECD is determined by measuring the projected area (the product of edge lengths) of the upper surface of each grain. From the grain projected area, the ECD of the grain is calculated. Grain thickness is commonly determined by oblique illumination of the grain population resulting in the individual grains casting shadows. From a knowledge of the angle of illumination (the shadow angle), it is possible to calculate the thickness of a grain from a measurement of its shadow length. The grains having square or rectangular faces and



each having a ratio of ECD/t of at least 2 are tabular grains having {100} major faces. The ratio of ECD/t is known as the "aspect ratio". When the projected areas of the {100} tabular grains account for at least 50% of total grain projected area, the emulsion is a tabular grain emulsion. Procedures for measuring ECD and t are well known in the art.

The minimum aspect ratio of the emulsions described herein is 2, but more typically, it is greater than or equal to 5. Preferably, it is at least 8 and more preferably, it is over 12. That is, preferred emulsions are high aspect ratio tabular grain emulsions. Higher aspect ratios, that is up to 200 or more can be realized, if desired. Emulsions within the scope of this invention in which the average aspect ratio approaches the minimum limit of 2 still provide a surface to volume ratio that is 200% that of cubic grains.

The tabular grain population can exhibit any grain thickness that is compatible with the average aspect ratios noted above. However, particularly when the selected tabular grain population exhibits a high average aspect ratio, it is preferred to additionally limit the grains included in the grain population to those that exhibit a thickness of less than 0.3 micrometers, and optimally, less than 0.2 micrometers. It is appreciated that the aspect ratio of a tabular grain can be limited either by limiting ECD or increasing its thickness. Thus, when the average aspect ratio of the tabular grain population is in the range of from 2 to 8, the tabular grains accounting for at least 50% of total grain projected area can also each exhibit a grain thickness of less than 0.3 micrometers. However, in the aspect range of from 2 to 8, thicker grains may be desirable.

Ultrathin grains may also be useful in certain elements. Such grains have an average thickness of less than 0.6 micrometers, and may have a thickness as low as 0.01 micrometers.

Another characteristic of tabular grains setting them apart from other emulsions is tabularity that can be defined as

$$T = \text{ECD}/t^2 = \text{AR}/t$$

wherein T is tabularity, AR is aspect ratio, ECD is equivalent circular diameter in micrometers, and t is thickness in micrometers. The predominantly chloride tabular grain population accounting for 50% or more of total grain projected area preferably exhibits a tabularity greater than 25 and more preferably, a tabularity greater than 100. Extremely high tabularities are contemplated as well since the grains can be ultrathin.

The tabular grain population can exhibit an average ECD of any photographically useful magnitude. For photographic utility, average ECD's of less than 10  $\mu\text{m}$  are contemplated, although average ECD's in most photographic applications rarely exceed 6 micrometers. Within ultrathin tabular grain emulsions, it is possible to provide intermediate aspect ratios with ECD's of the tabular grain population of 0.10 micrometers or less. As is generally understood by those skilled in the art, emulsions with selected tabular grain populations having higher ECD's are advantageous for achieving relatively high levels of photographic sensitivity while selected tabular grain populations with lower ECD's are advantageous in achieving low levels of granularity.

So long as tabular grains having the desired characteristics described above account for the requisite proportion of the total grain projected area, the remainder of the total grain projected area can be accounted for by any combination of coprecipitated grains. It is, of course, common practice in the art to blend emulsions to achieve specific photographic objectives. Blended emulsions in which at least one component emulsion satisfies the tabular grain descriptions noted above are specifically contemplated.

The particular details preparing the emulsions useful in the practice of this invention are provided in considerable detail in US-A-5,443,943, as well as considerable other photographic literature. Certain essential features are described herein as well.

The emulsions are obtained using a precipitation process in which nucleation occurs in a high chloride environment in the presence of iodide ion under conditions that favor the emergence of {100} crystal faces. As grain formation occurs, the inclusion of iodide into the cubic crystal lattice being formed by silver ions and the remaining halide ions is disruptive because of the much larger diameter of iodide ion as compared to chloride ion. The incorporated iodide ions introduce crystal irregularities that in the course of further grain growth result in tabular grains rather than regular (cubic) grains. It is generally preferred to maintain the iodide ion concentration in the dispersing medium during precipitation at the outset of nucleation at less than 10 mol%. Considerably lower amounts are also contemplated, including down to 0.001 mol% iodide ion.

In a preferred embodiment, silver iodochloride grain nuclei are formed during the nucleation step. Any amount of bromide ion can be present in the dispersing medium during nucleation that is compatible with at least 50 mol% of the halide in the grain nuclei being chloride ion.

Any convenient source of silver and halide ions can be employed during the nucleation step. Silver ion is preferably introduced as an aqueous silver salt solution, such as a silver nitrate solution. Halide ion is preferably introduced as an alkali or alkaline earth halide, such as lithium, sodium, potassium or calcium chloride, bromide or iodide. Other precipitation procedures, conditions (for example, temperature, pH, agitation,  $\Delta\text{VAg}$  and flow rate), amounts and components, including synthetic or natural peptizers, would be readily apparent to one skilled in the art. Particularly useful peptizers are gelatino peptizers such as gelatin and gelatin derivatives (such as low methionine gelatino peptizers). Alternative peptizers are the collagenlike synthetic biopolymers that have low binding affinity for silver ion (that is, a  $\Delta\text{VAg}$  of 50 mV

or less) and that can be prepared using genetic engineering techniques in yeast host cells.

A grain growth step follows nucleation in which the grain nuclei are grown until tabular grain having {100} major faces of a desired average ECD are obtained. Growing procedures, conditions, amounts and components are well known also that will increase the likelihood of obtaining predominantly tabular grains. Further details are described in US-A-5,443,943, noted above. Ripening agents, additional halides, peptizers, dopants, stabilizers, restraining agents (to restrain emergence of non-{100} grain crystal faces) and redox active species such as solubilized catechol derivatives can be introduced at the appropriate times in appropriate amounts as would be readily apparent to one skilled in the art.

It is also contemplated to deposit epitaxially silver salt onto the tabular grains acting as hosts. Conventional epitaxial depositions onto high chloride silver halide grains are illustrated, for example, in US-A-4,435,501 (particularly Example 24B), US-A-4,786,588, US-A-4,791,053, US-A-4,820,624 and US-A-4,865,962.

In a preferred embodiment of this invention, a method comprises processing an imagewise exposed and developed originating color photographic element that:

- a) has silver halide emulsions having a silver halide grain population wherein at least 50% of the total grain projected area is accounted for by tabular grains having an aspect ratio of at least 2 (preferably at least 8 and more preferably, at least 12) wherein the halide comprises at least 50 mol% chloride ion and less than 2% iodide ion, based on total silver, and
- b) is substantially free of a bleaching rate retarding amount of a development inhibitor having a free valence that binds to silver,

The method comprises bleaching the element with a bleaching solution comprising:

- a peroxide bleaching agent present in an amount of at least 0.5 mol/l, and
- chloride ion present in an amount of at least 0.35 mol/l.

More preferred embodiments are those in which the tabular grains are further characterized as having {100} major faces having adjacent edge ratios of less than 10, an aspect ratio greater than 2 and an average thickness of less than 0.35 micrometers.

While not preferred, the present invention can also be used to bleach elements having one or more tabular emulsions having {111} major faces. When such {111} tabular emulsions are used, it is preferred that they comprise a band region of higher iodide ion content surrounding a core region of lower iodide ion content since such banded structures provide for improved emulsion stability. Such {111} tabular emulsions are described, for example, in US-A-5,035,992 US-A-5,217,858 and US-A-5,389,509.

The photographic elements processed in the practice of this invention can be single or multilayer color elements. Multilayer color elements typically contain dye image-forming units sensitive to each of the three primary regions of the visible spectrum. Each unit can be comprised of a single emulsion layer or multiple emulsion layers sensitive to a given region of the spectrum. The layers of the element can be arranged in any of the various orders known in the art. In an alternative format, the emulsions sensitive to each of the three primary regions of the spectrum can be disposed as a single segmented layer. The elements can also contain other conventional layers such as filter layers, interlayers, subbing layers, overcoats and other layers readily apparent to one skilled in the art. A magnetic backing can be used as well as conventional supports.

Considerably more details of the element structure, components and photographically useful compounds (blocked or nonblocked), and suitable methods of processing various types of elements are described in *Research Disclosure*, noted above. All types of emulsions can be used in the elements, including but not limited to, thin tabular grain emulsions, and either positive-working or negative-working emulsions. The elements can be either photographic film or paper elements.

The elements are typically imagewise exposed to suitable radiation in the ultraviolet, visible (for example, actinic) or infrared regions of the electromagnetic spectrum to form a latent image and then processed to form a visible dye image. In addition, exposure can be accomplished using electron-beam and beta radiation, gamma ray, X-ray, alpha particle, neutron radiation and other forms of corpuscular and wave-like radiant energy in either noncoherent (random phase) or coherent (in phase) forms as produced by lasers. Exposure can be monochromatic, orthochromatic or panchromatic, continuous or intermittent, high- or low-intensity, long or short durations, and can occur at ambient, elevated or reduced temperatures and pressures.

Processing includes the step of color development in the presence of a color developing agent to reduce developable silver halide and to oxidize the color developing agent. Oxidized color developing agent in turn reacts with a color-forming coupler to yield a dye.

Color developers are well known and described in hundreds of publications including the *Research Disclosure*, noted above. In addition to color developing agents, the color developers generally contain a buffer (such as potassium

carbonate), a sulfite, chelating agents, halides, and one or more antioxidants as preservatives. There are many classes of useful antioxidants including, but not limited to, hydrazines and substituted or unsubstituted hydroxylamines. By substituted hydroxylamines is meant, for example, those having one or more alkyl or aryl groups connected to the nitrogen atom. These alkyl or aryl groups can be further substituted with one or more groups such as sulfo, carboxy, hydroxy, alkoxy and other groups known in the art which provide solubilizing effects. Examples of such hydroxylamines are described, for example, in US-A-4,876,174, US-A-4,892,804, US-A-5,178,992 and US-A-5,354,646. Two particularly useful antioxidants are N,N-bis(sulfonatoethyl)hydroxylamine, N-isopropyl-N-sulfonatoethylhydroxylamine, and salts thereof.

Development can also be carried out using what is known in the art as a "developer/amplifier" solution, as described in US-A-5,324,624.

Development is then followed by the use of a peroxide bleaching solution according to the practice of this invention. The bleaching step can be carried out in any suitable fashion, as is known in the art. Color prints and films can be processed using a wide variety of processing protocols, as described for example, in *Research Disclosure*, noted above, and thus can include various combinations of one or more bleaching, fixing, washing or stabilizing steps in various orders, and lastly, drying. Additionally, reversal processes include additional steps of black and white development, chemical fogging, re-exposure, and washing prior to color development.

Bleaching is generally carried out for less than 500 seconds, but longer times can be used if desired. Preferably, the bleaching time is from 15 to 480 seconds, and more preferably, it is from 120 to 240 seconds. Bleaching is generally carried out at a temperature that is at or above room temperature, for example from 20 to 50°C, and more preferably from 20 to 45°C.

Fixing following bleaching can be carried out using any suitable fixing solution containing one or more suitable fixing agents and other optional components (accelerators, buffers, preservatives and other components readily known to one skilled in the art). Particularly useful fixing agents are thiosulfates, such as sodium and ammonium thiosulfates, thioethers and thiourea. The amounts of fixing agents and suitable solution pH would be readily apparent to one skilled in the art. A particularly useful fixing solution comprises thiosulfate anion and sodium cation, and optionally a thioether accelerator. More particularly, these fixing solutions are substantially free of ammonium ion, and have a thiosulfate ion concentration of less than 0.8 mol/l.

Following fixing, the elements can be merely dried, or further processed using one or more washing, rinsing or stabilizing steps, using known procedures and solutions.

The times and temperatures for color development, fixing, stabilizing, washing or other steps of the method of this invention would be readily apparent to one skilled in the art.

Processing according to the present invention can be carried out using conventional processing equipment. Alternatively, it can be carried out using what is known in the art as "low volume thin tank" processing systems having either rack or tank or automatic tray designs. Such processing methods and equipment are described, for example, in US-A-5,436,118.

The following examples are presented to illustrate the practice of this invention. Unless otherwise indicated, all percentages are by weight.

#### **Materials and Methods for Examples:**

The following photographic elements were prepared using known materials in order to demonstrate the practice of this invention. The components not identified by name are described in published literature or references as noted in Table I below. The quantities of silver halide are given in grams of silver per m<sup>2</sup>. All other quantities are given in g/m<sup>2</sup>.

#### **Photographic Element 1:**

All of the development inhibitor releasing (DIR) compounds used in this element enable release of development inhibitors that have a free nitrogen valence that may bind to silver, and lack a free sulfur valence that binds to silver. The organic compounds were optionally coated in conventional coupler solvents or in conventional solutions as would be readily apparent to one skilled in the art. Such coupler solvents include tricresylphosphate, di-*n*-butyl phthalate, N,N-di-*n*-ethyl lauramide, N,N-di-*n*-butyl lauramide, 2,4-di-*t*-amylphenol, N-butyl-N-phenyl acetamide, di-*n*-butylsebacate and 1,4-cyclohexylene-diamethylene bis (2-ethoxyhexanoate). Element 1 also contained conventional amounts of sodium hexameta-phosphate, 1,3-butanediol, 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene and disodium-3,5-disulfocatechol.

The silver halide emulsions used in Element 1 were chemically and spectrally sensitized and selectively comprised a silver chloride region with a surrounding iodide band, using the teaching of US-A-5,314,798. The individual emulsions comprised 0.55 mol% iodide ion based on total silver. Conventional amounts of surfactants, coating aids, scavengers, soluble absorber dyes and stabilizers, as well as conventional levels of various iron, lead, gold, platinum, palladium, iridium and rhodium salts were included in the emulsions or other layers of the element. The total dry thickness of all applied layers on the transparent cellulose triacetate support was 18 µm, while the thickness from the innermost face

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of the sensitized layer closest to the support to the outermost face of the sensitized layer farthest from the support was 14  $\mu\text{m}$ .

The layers of Element 1 containing gelatin were hardened at coating with 2% of hardener to gelatin.

5 The following layers and components of Element 1 are listed below in order of layers closest to the cellulose triacetate support to the outermost layer:

### Antihalation Layer:

10 DYE-1 at 0.0108 g,  
DYE-2 at 0.022 g,  
C-39 at 0.097 g,  
DYE-6 at 0.108 g,  
DYE-9 at 0.075g,  
15 SOL-1 at 0.011 g,  
SOL-2 at 0.011 g, and  
Gelatin at 2.1 g.

### Lowest Sensitivity Red-Sensitive Layer:

20 Red sensitive silver chloride {100}-faced tabular emulsion, average ECD of 0.6  $\mu\text{m}$ , average thickness of 0.06  $\mu\text{m}$  at 0.140 g,  
C-1 at 0.538 g,  
D-32 at 0.015 g,  
C-42 at 0.097 g,  
25 ST-16 at 0.011 g,  
B-1 at 0.043 g, and  
Gelatin at 1.30 g.

### Medium Sensitivity Red-Sensitive Layer:

30 Red sensitive silver chloride {100}-faced tabular emulsion, average ECD of 1.0  $\mu\text{m}$ , average grain thickness of 0.1  $\mu\text{m}$  at 0.323 g,  
C-1 at 0.129 g,  
D-32 at 0.002 g,  
35 C-42 at 0.032 g,  
C-41 at 0.032 g,  
ST-16 at 0.011 g, and  
Gelatin at 0.59 g.

### Highest Sensitivity Red-Sensitive Layer:

40 Red sensitive silver chloride {100}-faced tabular emulsion, average ECD of 1.4  $\mu\text{m}$ , average grain thickness of 0.14  $\mu\text{m}$  at 0.70 g,  
C-1 at 0.043 g,  
45 D-32 at 0.002 g,  
C-42 at 0.022 g,  
C-41 at 0.011 g,  
ST-16 at 0.011 g, and  
Gelatin at 0.83 g.

### Interlayer:

50 ST-4 at 0.11 g, and  
Gelatin at 1.08 g.

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### Lowest Sensitivity Green-Sensitive Layer:

Green sensitive silver chloride {100}-faced tabular emulsion, average ECD of 0.6  $\mu\text{m}$ , average grain thickness of 0.06  $\mu\text{m}$  at 0.161 g,

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C-2 at 0.280 g,  
I-18 at 0.019 g,  
C-40 at 0.097 g,  
ST-5 at 0.056 g,  
ST-16 at 0.011 g, and  
Gelatin at 0.95 g.

### Medium Sensitivity Green-Sensitive Layer:

Green sensitive silver chloride {100}-faced tabular emulsion, average ECD of 0.9  $\mu\text{m}$ , average grain thickness of 0.09  $\mu\text{m}$  at 0.32 g,  
C-2 at 0.055 g,  
I-18 at 0.065 g,  
C-40 at 0.027 g,  
ST-5 at 0.011 g,  
ST-16 at 0.011 g, and  
Gelatin at 0.59 g.

### Highest Sensitivity Green-Sensitive Layer:

Green sensitive silver chloride {100}-faced tabular emulsion, average ECD of 1.4  $\mu\text{m}$ , average grain thickness of 0.14  $\mu\text{m}$  at 0.70 g,  
C-2 at 0.065 g,  
C-40 at 0.027 g,  
I-18 at 0.002 g,  
ST-5 at 0.011 g,  
ST-16 at 0.013 g, and  
Gelatin at 0.86 g.

### Interlayer:

DYE-7 at 0.075 g,  
C-39 at 0.032 g,  
ST-4 at 0.11 g, and  
Gelatin at 1.08 g.

### Lowest Sensitivity Blue-Sensitive Layer:

Blue sensitive silver chloride {100}-faced tabular emulsion with average ECD of 0.9  $\mu\text{m}$  and average grain thickness of 0.09  $\mu\text{m}$  at 0.161 g,  
Blue sensitive silver chloride {100}-faced tabular emulsion with average ECD of 1.4  $\mu\text{m}$  and average grain thickness of 0.14  $\mu\text{m}$  at 0.129 g,  
C-27 at 0.215 g,  
C-29 at 0.70 g,  
I-18 at 0.005 g,  
ST-5 at 0.011 g, and  
Gelatin at 1.51 g.

### Highest Sensitivity Blue-Sensitive Layer:

Blue sensitive silver chloride {100}-faced tabular emulsion with average ECD of 2.3  $\mu\text{m}$  and average grain thickness of 0.18  $\mu\text{m}$  at 0.86 g,  
C-27 at 0.043 g,  
C-29 at 0.129 g,  
I-18 at 0.002 g,  
ST-5 at 0.011 g, and  
Gelatin at 0.99 g.

Protective Layer 1:

5 DYE-8 at 0.11 g,  
DYE-9 at 0.11 g, and  
Gelatin at 0.7 g.

Protective Layer 2:

10 Silicone lubricant at 0.04 g,  
Tetraethylammonium perfluorooctane sulfonate,  
Silica at 0.29 g,  
Anti-matte polymethylmethacrylate beads at 0.11 g,  
Soluble anti-matte polymethylmethacrylate  
15 beads at 0.005 g, and  
Gelatin at 0.89 g.

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TABLE I

COMPOUND	LITERATURE SOURCE
DYE 1	US-A-5,443,943
DYE 2	"
DYE 6	"
DYE 7	"
DYE 8	"
DYE 9	"
C-1 coupler	"
C-2 coupler	"
C-15 coupler	"
C-27 coupler	"
C-29 coupler	"
C-39 dye releasing compound	"
C-40 dye releasing compound	"
C-41 dye releasing compound	"
I-18 DIR compound	1-18 of US-A-5,250,399
B-1 Bleach accelerator	US-A-5,443,943
D-1 DIR coupler	"
D-4 DIR coupler	"
D-8 DIR coupler	"
D-15 DIR coupler	"
D-16 DIR coupler	"
D-17 DIR coupler	"
D-20 DIR coupler	"
D-32 DIR coupler	"
ST-4	<i>Research Disclosure</i> publication 37038, 1995, pages 79-115
ST-5	"
ST-16	"
SOL-1	US-A-5,443,943
SOL-2	"

Photographic Element 2:

This element was prepared similarly to Element 1 identified above, using the conventional interlayers, subbing layers, antihalation layers and overcoat layers, stabilizers and addenda. The silver content was adjusted to maintain gamma. All of the DIR compounds were like those in Element 1. Only the different radiation sensitive layers of this element are listed as follows:

Red light sensitive color record:

Red sensitive silver chloride {100}-faced tabular emulsion, average ECD of 2.1  $\mu\text{m}$ , average grain thickness of 0.16  $\mu\text{m}$  at 0.54 g,

Red sensitive silver chloride {100}-faced tabular emulsion, average ECD of 1.0  $\mu\text{m}$ , average grain thickness of 0.10  $\mu\text{m}$  at 0.54 g,

C-1 at 0.646 g,

D-1 at 0.108 g, and

B-1 at 0.043 g.

Green light sensitive color record:

Green sensitive silver chloride {100}-faced tabular emulsion, average ECD of 2.1  $\mu\text{m}$ , average grain thickness of 0.16  $\mu\text{m}$  at 0.59 g,

Green sensitive silver chloride {100}-faced tabular emulsion, average ECD of 1.0  $\mu\text{m}$ , average grain thickness of 0.10  $\mu\text{m}$  at 0.59 g,

C-2 at 0.161 g,

C-15 at 0.269 g, and

D-4 at 0.097 g.

Blue light sensitive color record:

Blue sensitive silver chloride {100}-faced tabular emulsion, average ECD of 2.1  $\mu\text{m}$ , average grain thickness of 0.16  $\mu\text{m}$  at 0.39 g,

Blue sensitive silver chloride {100}-faced tabular emulsion, average ECD of 1.4  $\mu\text{m}$ , average grain thickness of 0.14  $\mu\text{m}$  at 0.39 g,

C-27 at 0.323 g,

C-29 at 0.646 g, and

D-4 at 0.108 g.

Photographic Element 3:

This element was similar to Element 2 except that in the red light sensitive color record, DIR coupler D-1 was replaced by DIR coupler D-15 at 0.065 g and DIR coupler D-17 at 0.065 g. Also, in the green light sensitive color record, DIR coupler D-4 was replaced by DIR coupler D-16 at 0.097 g, and in the blue light sensitive color record, DIR coupler D-4 was replaced by DIR coupler D-8 at 0.108 g. All of the Development Inhibitor Releasing (DIR) Compounds employed in this element enable release of development inhibitors having a free sulfur valence which may bind to silver. Thus, Element 3 is not useful in the practice of the present invention.

Photographic Element 4:

This element is also not useful in the practice of the present invention. It was similar to Element 1 except that, in the red light sensitive color record, DIR coupler D-32 was replaced by DIR coupler D-20 at 0.038 g, in the green light sensitive color record, DIR coupler I-18 was replaced by DIR coupler D-16 at 0.032 g and DIR coupler D-1 at 0.043 g, and in the blue light sensitive color record, DIR coupler I-18 was replaced by DIR coupler D-4 at 0.043 g. The silver content was adjusted to maintain gamma. The noted DIR Compounds employed in this element enable release of both development inhibitors having a free nitrogen valence which may bind to silver and development inhibitors having a free sulfur valence which may bind to silver.

Photographic Element 5:

This element is useful in the practice of this invention. It was like Element 1 except that the {100}-faced tabular silver chloride emulsions were each replaced by chemically and spectrally sensitized {111}-faced tabular silver chloride emulsions characterized in that the emulsions were precipitated in the presence of 7-azaindole and included an iodide band region near the grain surface which allowed removal of the stabilizer. The overall iodide content of each emulsion was 0.5 mol% based on total silver. Aim silver content was adjusted to maintain gamma.

Photographic Elements 1-5, described above, all showed a photographic sensitivity in excess of ISO-25 after imagewise exposure and photographic development. The following Table II summarizes the characteristics of the elements.



TABLE II

ELEMENT	SILVER LEVEL g/m <sup>2</sup>	EMULSION TYPE	DIR COMPOUND
1	3.50	{100} AgCl Tabular	Nitrogen-valence
2	3.14	"	"
3	"	"	Sulfur-valence
4	3.80	"	Nitrogen- & Sulfur-valence
5	3.42	{111} AgCl Tabular	Nitrogen-valence

The following bleaching solutions were prepared and used in the following examples. The concentrations of various components are listed in Table III below. All were prepared in a similar fashion by combining distilled water, 30% (w/w) hydrogen peroxide, sodium chloride, sodium carbonate and/or sodium bicarbonate, 1-hydroxyethylidene-1,1-diphosphonic acid (0.0042 mol/l final concentration), optionally 2,6-pyridinedicarboxylic acid (2,6-PDCA), and a small quantity of sodium hydroxide or sulfuric acid to adjust the final pH to 10.0 at 25°C. All of the bleaching solutions were colorless.

TABLE III

Bleaching Solution	Hydrogen peroxide (mol/l)	Chloride ion (mol/l)	Total carbonate (mol/l)	2,6-PDCA (mol/l)
A	0.98	0.35	0.05	--
B	0.33	0.35	0.05	0.035
C	0.33	1.00	0.05	0.035
D	0.33	0.35	0.50	0.035
E	0.33	1.00	0.50	0.035
F	0.98	0.35	0.05	0.035
G	0.98	1.00	0.05	0.035
H	0.98	0.35	0.50	0.035
I	0.98	1.00	0.50	0.035
J	0.65	0.68	0.28	0.035
K	0.49	1.00	0.50	0.035
L	0.74	0.35	0.05	--

#### **Example 1: Processing Elements Having {100} Faced Emulsion Grains Using Two Different Bleaching Solutions**

This example illustrates that complete bleaching without vesiculation is obtained using the present invention using two different peroxide bleaching solutions.

Samples (304.8 mm x 35 mm) of Element 1 were exposed at 1/50 second to a step wedge test object using a DLVa filter and 3000K illumination on a conventional 1B sensitometer, and processed at 37.8°C using the following protocol:

Developing*	90 seconds
Stop bath **	60 seconds
Washing ***	60 second
Bleaching (Solution A or L)	0, 240 seconds
Washing ***	180 seconds
Fixing #	240 seconds
Washing ***	180 seconds
Rinsing @	60 seconds

\*Color developing was carried out using a solution of conventional KODAK FLEXICOLOR Developer.

\*\*The Stop bath contained concentrated sulfuric acid (10 ml/l).

\*\*\*Washing was carried out using water.

#Fixing was carried out using conventional KODAK FLEXICOLOR Bleach.

@Rinsing was carried out using conventional KODAK PHOTO-FLO (5 ml/l).

Bleaching solutions A and L are described above. Both fall within the scope of the present invention. Residual silver was measured in steps 1, 2, 3, 11, 19, 20, and 21 by conventional X-ray fluorescence techniques, and the results are shown below in Table IV. The data make it clear that bleaching was complete ( $\cong 0.05 \text{ g/m}^2$  residual Ag) using both bleaching solutions. Careful visual inspection of the film samples indicated no vesiculation in the bleached elements.

TABLE IV

STEP NUMBER	RESIDUAL SILVER (g/m <sup>2</sup> )		
	NO BLEACHING	BLEACHING SOLUTION A	BLEACHING SOLUTION L
1	1.50	0.03	0.04
2	1.45	0.01	0.04
3	1.39	0.01	0.03
11	0.54	0.00	0.02
19	0.16	0.00	0.01
20	0.16	0.00	0.00
21	0.16	0.00	0.00

#### **Example 2: Criticality of Element and Bleaching Solution in Processing Elements Having {100} Faced Tabular Grain Emulsions**

This example illustrates the criticality of peroxide and chloride concentrations in the bleaching solution, as well as the criticality of the type of development inhibitor in the element, in achieving complete bleaching without vesiculation according to the present invention. It further supports the preference for chloride concentrations greater than 0.5 mol/l.

Samples (304.8 mm x 35 mm) of Elements 2, 3 and 4 described above were exposed at 1/25 second to a step wedge test object using a DLVa filter and 3000K illumination on a conventional 1B sensitometer, and processed at 37.8°C using the protocol of Example 1, except that the color developer was conventional KODAK EKTACOLOR RA

Developer, and bleaching solutions B-J were used. Conventional X-ray fluorescence spectroscopy was used to determine the residual silver in exposure steps 2, 3 and 4, and the resulting values were averaged to give the reported values of residual Dmax silver. Table V below lists these data and observations regarding vesiculation.

It is apparent that Element 3, which is outside the scope of this invention (all of the DIR couplers release development inhibitors with free sulfur valence), was inadequately desilvered using all bleaching solutions tested. Element 2, which is free of development inhibitors with free sulfur valence and thus within the scope of this invention, was acceptably desilvered using bleaching solutions F-J, which contained either 2 or 3% peroxide. Of those bleaching solutions, there is a preference for those with chloride concentrations greater than 0.35 mol/l because of their greater ability to control vesiculation (for example, for Element 2, there is a preference for bleaching solution G over bleaching solution F, and bleaching solution I over bleaching solution H).

Element 4, in which there is a mixture of DIR couplers with and without development inhibitors with free sulfur valence, was inadequately desilvered using both bleaching solutions tested. Thus both the type of DIR compound in the element and the concentration of chloride and peroxide in the bleaching solution are critical to achieving complete desilvering without vesiculation in the practice of this invention.

TABLE V

ELEMENT	BLEACHING SOLUTION	RESIDUAL DMAX SILVER (g/m <sup>2</sup> )	VESICULATION	WITHIN INVENTION?
2	B	0.817	None	No
2	C	0.085	None	No
2	D	0.063	None	No
2	E	0.831	None	No
2	F	0.015	Steps 1-4	Yes
2	G	0.031	None	Yes
2	H	0.024	Steps 1-5	Yes
2	I	0.029	None	Yes
2	J	0.039	None	Yes
3	B	0.740	None	No
3	C	0.381	None	No
3	D	0.368	None	No
3	E	0.740	None	No
3	F	0.099	Steps 1-4	No
3	G	0.174	Steps 1-3	No
3	H	0.203	Steps 1-8	No
3	I	0.195	Steps 1-6	No
3	J	0.253	None	No
4	K	0.175	None	No
4	I	0.080	Steps 1-8	No

### Example 3: Processing Element with {111} Tabular Silver Chloride Emulsions

This example demonstrates the practice of this invention to process elements having the less preferred {111} faced tabular grain emulsions.

Samples (304.8 mm x 35 mm) of Element 5 were exposed and processed using Bleaching solution H and the protocol described in Example 2. Residual silver and vesiculation were evaluated as a function of bleaching time as described in Example 2. The data are presented in Table VI below. After 240 seconds of bleaching, the element sam-

ples were desilvered, and no vesiculation was evident.

TABLE VI

BLEACHING TIME (SEC)	RESIDUAL DMAX SILVER (g/m <sup>2</sup> )	VESICULATION
0	2.277	--
15	1.540	None
30	0.796	None
45	0.545	None
60	0.423	None
90	0.312	None
120	0.217	None
180	0.137	None
240	0.086	None

#### Claims

1. A method for processing an imagewise exposed and developed originating color photographic element that:

- a) has at least one silver halide emulsion layer having predominantly chloride ion as the halide, and less than 2% iodide ion, based on total silver halide, and
- b) is substantially free of a bleaching rate retarding amount of a development inhibitor having a free valence that binds to silver,

the method comprising bleaching the element with a bleaching solution comprising:

a peroxide bleaching agent present in an amount of at least 0.35 mol/l, and  
chloride ion present in an amount of at least 0.35 mol/l.

2. The method as claimed in claim 1 wherein chloride ion is present in the bleaching solution in an amount of from 0.35 to 1 mol/l.

3. The method as claimed in either claim 1 or 2 wherein the peroxide is hydrogen peroxide present in an amount of from 0.6 to 2.5 mol/l, and the chloride ion is present in the bleaching solution in an amount of from 0.35 to 0.75 mol/l.

4. The method as claimed in any of claims 1 to 3 wherein the bleaching solution further comprises an organic phosphonic acid, organic carboxylic acid, or salt thereof, in an amount of at least 0.0005 mol/l.

5. The method as claimed in any of claims 1 to 4 wherein the predominantly chloride silver chloride emulsion layer has at least 50% of the total grain projected area accounted for by tabular grains having an aspect ratio of at least 2, and at least 50 mol% chloride silver halide and the tabular grains are further characterized by having {100} major faces having adjacent edge ratios of less than 10.

6. The method as claimed in claim 5 wherein the tabular grains have been nucleated in the presence of iodide ion.

7. The method as claimed in claim 5 wherein the tabular grains have an average thickness of less than 0.35 micrometers.

8. The method as claimed in any of claims 1 to 7 wherein the originating photographic element has a silver coverage of from 1 to 4 g Ag/m<sup>2</sup>.

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9. The method as claimed in any of claims 1 to 8 wherein the predominantly chloride silver halide emulsion layer has at least 70% chloride ion based on total silver halide.
10. The method as claimed in any of claims 1 to 9 wherein the element has a light sensitivity of at least ISO 25.

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# EUROPEAN SEARCH REPORT

Application Number  
EP 96 10 7998

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP-A-0 428 101 (FUJII PHOTO FILM CO LTD) 22 May 1991 * page 3, line 25 - page 4, line 3 * * claim 1 * * Page 51, Table 1, Runs 8 and 9 * * page 10, line 25 - line 36 * ---	1,2,4,9	G03C7/42
A	WO-A-92 07300 (KODAK LTD ;EASTMAN KODAK CO (US)) 30 April 1992 * page 3, line 1 - line 3; claims 1-4,8 * ---	1-10	
A	US-A-4 454 224 (BRIEN GERALD J ET AL) 12 June 1984 * column 2, line 6 * * column 2, line 28 - line 68 * * column 3, line 58 - line 68; claim 1 * ---	1-10	
A	US-A-4 277 556 (KOBOSHI SIGEHARU ET AL) 7 July 1981 * column 6, line 34 - line 52; claim 1 * ---	1-10	
A	US-A-4 301 236 (IDOTA YOSHIO ET AL) 17 November 1981 * column 7, line 45 - line 62 * -----	1-10	<b>TECHNICAL FIELDS SEARCHED (Int.Cl.6)</b> G03C
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>1 October 1996</b>	Examiner <b>Bolger, W</b>
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

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